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(71) Applicant: FRATELLI LAMBERTI S.p.A.
Via Piave 18
I-21041 Albizzate (Varese)(IT)

(72) Inventor: Li Bassi, Giuseppe
Via Stretti, 4
I-21026 Gavirate (Varese)(IT)
Inventor: Nicora, Carlo
Via Filzi, 2
I-21100 Varese(IT)

(74) Representative: Gervasi, Gemma et al
NOTARBARTOLO & GERVASI Srl Viale
Bianca Maria 33
I-20122 Milan(IT)

(54) Aqueous disperse systems of photoinitiators and their use.

(57) The invention relates to aqueous disperse systems of photoinitiators which are particularly useful in the photopolymerisation of aqueous disperse systems and emulsions of oligomers or polymers carrying photopolymerisable functionalities which are widely used in the field of dyes and packaging.

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AQUEOUS DISPERSE SYSTEMS OF PHOTOINITIATORS AND THEIR USE

Field of the invention

The present invention relates to aqueous disperse systems of photoinitiators which are particularly useful in the photopolymerisation of aqueous systems comprising oligomers or polymers carrying photopolymerisable functionalities.

These aqueous systems, which are largely used in the field of dyes and in the coating of wrappings are normally constituted by aqueous emulsions and/or dispersions of polyurethanes, polyesters, polyethers, polyols, polyacrylates as oligomers and/or polymers carrying acrylic- and metacrylic-, fumaric-, maleic-, vinyl-ethers unsaturations.

Technical Problem

The photopolymerisable systems commonly used in industry are constituted by oligomers and/or polymers carrying functionalities which can polymerise or copolymerise when are diluted in the appropriate reactive solvents.

With the expression reactive solvents are intended monomers having low molecular weight possessing various functionalities which have a good solving power and can therefore dissolve the oligomers and maintain the systems to a degree of viscosity appropriate for their use and which at the end of the polymerisation process remain included in the mass as integrant part of the polymeric matrix. Unfortunately the photoinitiate polymerisation, which is a very efficient process, does not permit the complete reaction of the monomer, and therefore the tecnical problem arises that the monomer can migrate and be extracted from the materials which come into contact with the photopolymerised masses.

In view of the toxicity and unpleasant smell of the solvents commonly used, it is easy to understand the importance of this technical problem which entails a strong limitation of the possible use of this technology in very important fields like the coating of food-wrappings (direct or indirect) and the painting and finishing of those materials which come into contact with the users.

State of the art

In the last times various possible solutions in alternative to the photopolymerisable systems comprising the dilution in reactive solvents have been studied.

Such solutions involve the use of oligomers or polymers carrying photopolymerisable functionalities which are dispersed or emulsifyed in water or if required diluted with water.

With these systems it is possible to perform the photopolymerisation either immediately after the application of the liquid system or after having evaporated the water.

In the case of aqueous emulsions or dispersions wherein the dry part represents 70-80% it is necessary to evaporate the water in order to obtain the coalescence of the system before performing the photopolymerisation on the resulting homogeneous film.

Although it is necessary to add one further step to the process for preparing the final products (i.e. the water evaporation) in respect of the traditional processes, the use of aqueous systems is widely spreading because it offers the advantage of avoiding the presence of inflamables monomers in the compositions on sale and also assures the absence of residue monomers in the final products. Anyhow, till now it has not been possible to solve satisfactorily the problems deriving from the use of the photoinitiators in aqueous systems.

The normally used photoinitiators can not be easily included in systems dispersed in water. This disadvantage is particularly relevant with solids as for example: benzyl-dimethyl-ketal, benzophenone and 1-benzoyl-cyclohexanol.

Normally the problem is avoided using liquid photoinitiators which are included in the aqueous dispersions or emulsions before their use. However the possibility of using only liquid photoinitiators represents a strong limitation since the users normally need a large flexibility to satisfy their various demands which request the employ of various photoinitiators.

In other cases the photoinitiator is dissolved in the photopolymerisable mixture before its emulsion with water at the moment of use (autoemulsifying mixtures), but this solution involves a complicated process of

production and therefore is not appreciated by the users.

In still other cases the photopolymerisable mixture are delivered to the user with the photoinitiator already included.

These mixtures, which do not require further manufacture, present the the disadvantage of a limited possibility of application since it is impossible to proportion or change the photoinitiator included during the production of the mixture.

Tipical examples of photoinitiators used in aqueous systems are 2-hydroxy-2-methyl-1-(p-dodecyl)-propiophenone as described in the EPA-85,305, wherein the introduction of an aliphatic chain in the molecule, for lowering the melting point of the product under the room temperature, results in a dilution of its part active as photoinitiator and therefore reduces its efficacity in respect of the compound not presenting the lateral dodecyl-chain; or the 2-hydroxy-2-methyl-1-phenyl-propiophenone described in the USA Patent 4,347,111, which is too volatile and is therefore easily lost during the coalescence-process by evaporation of the aqueous phase; or again the 2-hydroxy-2-methyl-1-(4-hydroxy-ethoxy-phenyl)-propiophenone, as described in the PCT-WO-86/05778, which is hydrophylic up to a certain degree but is obtained through a synthetic process, which is very complicated and therefore involves higher costs than those of other commonly used photoinitiators and therefore its use is limited.

Unfortunately, considering that the photopolymerisation process takes place in an organic-phase (after coalescence) it is not profitable to use photoinitiators which are soluble in water. This kind of photoinitiators are not very compatible with the organic matrix of the systems to photopolymerize and therefore the results are not satisfying.

Detailed description of the invention

We have now found that it is possible to use the photoinitiators normally used in non aqueous photopolymerisable systems also for aqueous systems when such photoinitiators are used as emulsions and/or disperse systems in water.

In the present text the term "disperse systems" means both disperse systems and emulsions.

According to a fundamental characteristic of the present invention the aqueous disperse systems of photoinitiators comprise at least a photoinitiator and at least a surface active agent.

The aqueous disperse systems of photoinitiators according to the present invention are stable, easy to proportion and to include in the mixtures of oligomers or polymers which must be polymerised and with which they do not interfere electrokinetically.

Such disperse systems of photoinitiators can have anionic, cationic or non-ionic character according to the surface active agents used. Normally it is preferable to use non-ionic aqueous disperse systems of photoinitiators because they are more compatible with all the photopolymerisable systems dispersed in water.

The aqueous disperse systems of photoinitiators according to the present invention can contain a single photoinitiator or a mixture of them or also a couple of a photoinitiator and an hydrogen-donor (co-initiator).

Among the photoinitiators useful for the aqueous disperse systems according to the present invention are benzoin ethers, benzyldimethylketal, 2,2-dialkoxy-acetophenones, alpha-hydroxy-alkyl-aryl ketones, aryl-glyoxylic acid esters, mono- and di-acyl-phosphine oxides, aromatic ketones, especially benzophenone, tioxanthones, antraquinones or the esa-aryl-bis-imidazoles.

As co-initiators can be used the compounds having a tertiary amino group with at least an hydrogen atom on the carbon atom linked to the nitrogen of the amino group.

If the above said compounds are soluble in water, as for example the N-methyl-N,N-diethanolamine (MDEA) or the triethanolamine, they can also be added to the mass to polymerise instead of being added to the aqueous dispersion of the photoinitiator without presenting negative effects on the photopolymerisation reaction. On the other hand it is preferred to add to the aqueous dispersion of the photoinitiator, and especially during its preparation, those compounds which are not soluble in water, as for example the esters of p-dimethylammino-benzoic acid.

The tipical ratio in weight of photoinitiators and co-initiators in the aqueous disperse systems according to the present invention is comprised between 1:1 and 1:2.5.

The surface active agents in the aqueous disperse systems according to the present invention have an emulsifying action, helping the wettability of the compounds to disperse in water, and also a dispersing action, preventing to reaggregate the drops of the dispersed phase.

All the surface active agents normally available on the market can be used for the disperse systems according to the present invention, particularly suitable are the organic sulphonic acids and their salts,

mono-alkyl-sulphates, quaternary ammonium salts, higher aliphatic alcohols or alkyl-phenoles condensed with ethylene oxide and/or propylene, partial esters of phosphoric acid with aliphatic alcohols and their salts.

In the preferred embodiments of the aqueous disperse systems of photoinitiators according to the invention one or more dispersions stabilizers are added.

Such stabilizers have a thickening action and impart to the dispersion pronounced thixotropic and pseudoelastic characteristics, with high stand viscosity and a viscosity proportionally decreasing with the increasing of the mechanical stress to which the disperse system is subjected.

Among the substances having a stabilizing action useful in the aqueous disperse systems according to the present invention, are particuarly preferred the polymers and the copolymers of acrylic and metacrylic acid, maleic anhydride, polyvinylalcohol, ionic and non-ionic derivatives of cellulose and natural polysaccharides, among which particularly preferred are xanthane and its derivatives.

The quantities of the various components the aqueous disperse systems of photoinitiators according to the present invention can vary in wide ranges always maintaining their efficiency.

According to a fundamental characteristic of the present invention the photoinitiator (or the mixture of photoinitiators in the case that more then one are used) represents from 20% to 80% by weight of the disperse system and the surface active agent represents from 0.1% to 10% by weight.

In the preferred embodiments of the invention, the photoinitiator, or the mixture of photoinitiators, represents from 30% to 60% by weight and the surface active agent from 0.5% to 2% by weight of the disperse system.

When one or more stabilizers are added to the aqueous disperse system of the photoinitiator, their concentration is preferably comprised between 0.1 and 2% by weight of the aqueous disperse system.

In the above described range of concentrations, the aqueous disperse systems of photoinitiators according to the present invention are stable, either in respect of viscosity or phase separation, and can be easily stored and put on the market.

Their compatibility with the common aqueous systems of oligomers and/or polymers on the market is excellent and allows their inclusion in all the known aqueous systems.

The aqueous disperse systems of photoinitiators according to the present inventions can also include other substances, over those already mentioned, which can help in their production or prevent their deterioration as for example antifoam, degasing, antibacterial and antimold agents.

It is also possible to add to the aqueous disperse systems according to the invention all those auxiliaries which are commonly used in the aqueous systems which must be photopolymerised as thermic stabilizers, spreader, coalescence auxiliaries, pigments, photostabilizers.

The aqueous dispersions according to the invention can be prepared according to the usual dispersing techniques, in particular by mechanical action with fast agitators or colloid mills.

The inclusion of the aqueous disperse systems of photoinitiators according to the invention in the aqueous systems which must be photopolymerised is performed by mixing under mild mechanical action.

The employing ratios between the photoinitiating dispersion and the aqueous system are based on the ratios of their dry parts. Normally the qualitity of photoinitiator used is comprised between 0.5% and 10% by weight in respect of the oligomer and/or polymer contained in the system to photopolymerise.

The liquid compositions obtained after the mixing of the aqueous dispersion of photoinitiator and the aqueous system to photopolymerise are stable and can be easily stored if not immediately used and put on the market.

The composition obtained can be applied in the usual way by rolling, spraying, curtain-spraying, brushing, blading, if necessary after thickening.

The liquid film, however applied, is subjected to fast heating to evaporate the aqueous phase and produce the coalescence and afterwards is crosslinked by irradiation with UV-lamps.

In some cases the heat of the lamps used for the crosslinking is sufficient to obtain the coalescence of the liquid film.

In the following examples all the parts are in weight if not otherwise specified.

The substaces used in the examples are available on the market under the following trading names :

ESACURE (F.lli Lamberti Spa)
SARTOMER (Sartomer Co. USA)
PROXEL (ICI)
RHODOPOL (Rhône-Poulenc)
LAROMER (BASF)
IRGACURE (Ciba-Geigy)
DAROCURE (Merck)
QUANTACURE (Ward Blekinsop)

NEOREZ (PolyvinylChemie)
ACRONAL (Rohm & Haas)
TEXANOL (Kodak)
PRESANTIL (F.lli Lamberti)
ESAPAL (F.lli Lamberti Spa)

EXAMPLE 1

To 65 parts of ESACURE KIP [75% of oligo-(4-alpha-hydroxy-isobutirryl)-alpha-methyl-styrene in diacrylated tripropylen-glycol] are added at 75° C 2 parts of nonylphenol condensed with 3 moles of ethylene oxide and 1 part of nonylphenol condensed with 9 moles of ethylene oxide, 0.2 parts of nonylphenol condensed with 100 moles of ethylene oxide, 1 part of N-methyldiethanolamine and 0.1 part of dodecyl alcohol condensed with 225 moles of ethylene oxide.

To the homogeneous solution are added 50 parts of water and 10 parts of polyethyleneglycol 400 diacrylated (SARTOMER SR 344). The suspension is grinded for 10 minutes in a colloidal mill Ultraturrax cooling from 75° C to 30° C. At the end are added under agitation 0.4 parts of PROXEL GXL (ICI) and 13 parts of an aqueous solution 2.27% in weight of RHODOPOL 23.

The dispersion obtained contains 34% in weight of alphahydroxyketonic oligomeric photoinitiator and has the following characteristics :
Appearance : Liquid dispersion, viscous, homogeneous, white
Viscosity : 2300 mpas at 20° C (Brookfield RVT 20 rpm)
Stability : Stable for more than 4 months at 40 ° C

EXAMPLE 2

To 65 parts of ESACURE KB1(Benzyl-dimethyl-ketal) are added at 75° C 1 part of nonylphenyl condensed with 9 moles of ethylene oxide, 2 parts of nonylphenol condensed with 3 moles of ethylene oxide, 1 part of of sulphated sodium salt of nonylphenol condensed with 30 moles of ethylene oxide, 1 part of 2-ethyl-hexanoic acid. To the homogeneous solution are added under agitation 100 parts of deionized water and the mixture is grinded for 10 minutes in Ultraturrax cooling to 35° C. At the end are added under agitation 0.4 parts of PROXEL GXL (ICI) and 8 parts of an aqueous solution 2.27% by weight of RHODOPOL 23.

The dispersion obtained contains 34.5% by weight of benzyldimethylketal and has the following characteristics :
Appearance : Dispersion having pastous consistency, homogeneous, white color.
Viscosity : 5000 mpas at 20° C (Brookfield RVT 20 rpm)
Stability : Stable for more than 4 months at 40 ° C

EXAMPLE 3

To 94.5 parts of ESACURE TZT (80 parts of 2,4,6-trimethylbenzophenone and 20 parts of methylbenzophenone) are added 1.5 parts of ESAPAL NP 90 (nonylphenol condensed with 9 moles of ethylene oxide), 0.75 parts of nonylphenol condensed with 100 moles of ethylene oxide, 0.3 parts of dodecyl- alcohol condensed with 225 moles of ethylene oxide and 6 parts of N-methyl-diethanolamine. To the homogeneous solution are added under agitation 95 parts of deionized water. The mixture is grinded for 10 minutes in a colloidal mill Ultraturrax) without passing 35° C. At the end are added under agitation 0.75 parts of PROXEL GXL (ICI) and 19 parts of an aqueous solution 2.27% by weight of RHODOPOL 23.

The dispersion obtained contains 44% by weight of photoinitiator and has the following characteristics :
Appearance : White, homogeneous, milky liquid
Viscosity : 900-1000 mpas at 20° C (Brookfield RVT 20 rpm)
Stability : Stable for more than 4 months at 40° C

EXAMPLE 4

The dispersion of benzophenone is obtained in an analogous manner as described in Example 3. The solution of the auxiliaries and the grinding in the colloidal mill Ultraturrax are performed at 60° C. The final characteristics of the dispersion are similar to those of the dispersion of the Example 3.

EXAMPLE 5

To 100 parts of LAROMER PE 55 W (acrylated polyester by BASF; pH 4.5-5, viscosity 1000 mpas, dispersion at 50% in water) are added the photoinitiators according to the quantities reported in TABLE 1 so that in all cases 1.5 parts of photoinitiatotor (100% active) on 100 parts of resin are present.

After agitation for 10 minutes, the composition is applied to a glass plate to a thickness of 100 micrometers. The plate is heated in oven at 100° C for 10 minutes and after cooling to ambient temperature is irradiated by passing it at 20 m/min under an 80 W Hanovia 6512-A-431 lamp, distance from the lamp 10 cm, for so many times as necessary for obtaining a tack free surface. The following characteristics are reported :

- reactivity (number of passages for obtaining a tack free surface)
- film appearance
- film color
- film residual smell

TABLE 1

Photoinitiator	parts % on system	n.pass.	Appearance	Yellowing (ASTM D 1925)	Smell
I (*)					
Product of Example 2	4.5	1	transp.	12	v.light
BDMK	1.5	2	transp.	12	v.light
Product of Example 1	4.4	1	transp.	8	absent
ESACURE KIP (1)	2.0	1	transp.	8	absent
IRGACURE KIP 184 (2)	1.5	3	transp.	8	aromat.
DAROCURE 1173 (3)	1.5	3	transp.	8	absent
DAROCURE 953 (4)	1.5	2	transp.	8	absent
II (*)					
QUANTACURE QTX (5)	1.5	2	transp.	18	aminic
QUANTACURE BTC (6)	1.5	3	opaque	12	aminic
Product of Example 3	3.5	1	opaque	10	absent
ESACURE TZT (7)	1.5	2	opaque	10	absent
Product of Example 4	3.5	1	opaque	10	absent
BZO	1.5	3	opaque	10	absent

(*) Photoinitiator by homolitic cleavage (fragmentation)

(**) " " hydrogen extraction. In each formulation are added also 1.5 parts of N-methyldiethanolamine for 100 parts of system

(1) oligo (4-alpha-2-hydroxyisobutirryl)-alpha methylstyrene, 75% in tripropyleneglycol diacrylate (Lamberti)

(2) 1-benzoylcyclohexanol (Ciba-Geigy)

(3) 2-hydroxy-2-methylpropiophenone (Merck)

(4) 2-hydroxy-2-methyl-1-(p-dodecyl) propiophenone (Merck)

(5) 2-hydroxy-3-(3,4-dimethyl-9-oxo-9H-tioxanthen-2-yloxy)-N,N,N-trimethyl-1-propan chloride (Ward Blekinsop)

(6) 4-benzoyl-benzyl-N-trimethyl chloride (Ward Blenkinsop) (photoinitiator soluble in water)

(7) 80% 2,4,6-Trimethylbenzophenone / 20% methylbenzophenone (Lamberti)

BDMK : Benzyldimethylketal

BZO : benzophenone

The example shows that the dispersed photoinitiators prepared as described in the examples 1 - 4 are all very active and do not present side disadvantage. ESACURE KIP is very active. The others photoinitiators of Group II are very yellowing and not compatible (QUANTACURE QTX and BTC) or slightly active (BZO).

Example 6

To 100 g of NEOREZ KT 18C (aliphatic acrylated polyurethane as aqueous dispersion 38%, pH 7, viscosity: 26 mpas) are added various amounts of the photoinitiators indicated in Table 2 (in order to have 1.5 parts of photoinitiator, at 100% of active, for 100 parts of resin in each preparation) and the mixture is stirred (60 rpm with impeller) for a fixed time, after that a film to a thickness of 200 micrometers (wet) is applied to a glass plate.

The plate is dried at 110°C for 5 minutes or for 20 minutes and is irradiated under an 8,10 W Hanovia 6512-A-431 lamp at 15 m/min. by two passages at 10 cm from the lamp.

The resistence to MEK (number of double rubs) on crosslinked films is measured.

TABLE 2

Photoinitiator	Parts % on System	5				20 Dry. (min)
		1	2	5	20	5 Stir. (min)
I(-)						
Products of Example 1	4.4	90	>200	180	180	178
ESACURE KIP	2.0	70	133	155	155	160
IRGACURE 184	1.5	30	40	25	30	77
DAROCURE 1173	1.5	40	40	40	40	40
Product of Example 2	4.5	164	130	190	185	185
BDMK	1.5	18	17	26	28	35
II (--)						
Product of Example 3	3.5	50	75	85	85	83
ESACURE TZT	1.5	30	62	76	75	78
Product of Example 4	3.5	48	70	82	80	81
BZO	1.5	25	60	75	72	72

(-) Photoinitiator by homolitic cleavage (fragmentation)
(--)Photoinitiator by hydrogen extraction. In each formulation are added also 1.5 parts of N-methyldiethanolamine for 100 parts of system.

The example shows that, given the same concentration, the photoinitiators as aqueous dispersion impart to the photopolymerisable system an higher photochemical reactivity, in respect to those normally available on the market. It is also demonstrated that, even after long mixing times, the normal photoinitiators are not suitable for use in these systems, while with the aqueous dispersions of photoinitiators already after few minutes of agitation interesting properties are obtained.

Even after longer drying times the normal photoinitiators do not impart to the films the wanted reactivity.

EXAMPLE 7

To 100 g of LAROMER PE 55 W (BASF, see example 5) are added various quantity of the photoinitiators indicated in TABLE 3 and the mixture is subjected to mechanical agitation (80 rpm, impeller) for 1.2 and minutes. The dispersion is applied on glass to a thickness of 200 micrometers (wet) and dried in oven at 120° C for 7 minutes.

After cooling it is irradiated under an 80 W Hanovia 6512-A-431 lamp at 20 m/min at 10 cm from the lamp.

The reactivity (number of passages for obtaining a tack free surface) (see Table 3) and film hardness (at the maximum dosage of luminous energy received) according to the method of Koenig's Pendulum (DIN 53157) in seconds (see Table 4) are measured.

The results reported in Table 3 show that, given the same concentration, the aqueous dispersed photoinitiators impart to the photopolymerisable system an higher reactivity in respect of the commercially available photoinitiators, independently from agitation time in the preparation of the mixtures. That means that the dispersions according to the present invention are highly compatible and easily included with a minimum of agitation. In this case also ESACURE KIP is very active since already diluted in diacrylated tripropylenglycol which promotes the dispersion.

The results reported in Table 4 show that for the photoinitiators in aqueous dispersion the films hardness is higher than that obtained using the corresponding pure photoinitiators (with the only exception of ESACURE KIP for the reasons given in the above mentioned table). In so far as the compounds of group I are concerned, the hardness with the pure products is lower even after longer irradiation times (3 passages instead of 2).

The same behaviour is noticed with the photoinitiators of group II, although, as it can be expected for

the hydrogen extraction systems, the hardness is inferior than that measured with the photoinitiators by fragmentation.

TABLE 3

number of passages for a tack-free surface					
Photoinitiator	parts % on system	1	2	5	agitation (min)
I (*)					
Product of Example 1	4.4	1	1	1	
ESACURE KIP	2.0	2	1	1	
IRGACURE 184	1.5	3	2	2	
DAROCURE 173	1.5	3	2	3	
Product of Example 2	4.5	1	1	1	
BDMK	1.5	3	2	2	
II(**)					
Product of Example 3	3.5	1	1	1	
ESACURE TZT	1.5	3	3	2	
Product of Exmple 4	3.5	1	1	1	
BZO	1.5	5	5	4	

(*) Photoinitiator by homolitic cleavage (fragmentation)
(**)Photoinitiator by hydrogen extraction. In each formulation are added also 1.5 parts of N-methyldiethanolamine for 100 parts of system.

Table 4

Hardness (Koenig's pendulum) (sec)					
Photoinitiator	Parts % on system	Number of passages	Agitation (min)		
			1	2	5
Product of Example 1	4.4	2	27	27	31
ESACURE KIP	2.0	2	27	28	27
IRGACURE 184	1.5	3	21	23	28
DAROCURE 173	1.5	3	11	18	25
I_a (-)					
Product of Example 2	4.5	2	22	22	29
BDMK	1.5	2	22	22	29
II(--)					
Product of Example 3	3.5	3	18	19	19
ESACURE TZT	1.5	3	15	16	16
II_a(--)					
Product of Example 4	3.5	5	11	11	11
BZO	1.5	5	9	9	9

(-) Photoinitiator by homolitic cleavage (fragmentation)
(--)Photoinitiator by hydrogen extraction. In each formulation are added also 1.5 parts of N-methyldiethanolamine for 100 parts of system

EXAMPLE 8

A water-paint for mural application is prepared by dispersing with a turbomixer "Molteni" (500 rpm) the following compounds in the given order (all the parts are by weight):

Base	
Water	parts 21.2
Sodium Hexametaphosphate	parts 1
Acrylic disperdent	parts 0.2
Antifoam	parts 0.1
Rutile titanium bioxide	parts 15
Calcium carbonate	parts 15
Talc	parts 4
ACRONAL 290 P (Rhom-Haas)	parts 35
PRESANTIL (Antiflash rusting)	parts 0.7
Diurethane thickener (20% in water)	parts 1
Ethylene glycol	parts 1
Coalescence agent (Texanol-Kodak)	parts 0.5
Antifoam	parts 0.2
Acrylic thickener	parts 2.4
Ammonia 28 Bè	parts 0.3
The formulation is completed by adding under mild agitation for 5 minutes (60 rpm) the other components.	

Finished	
Base	parts 10
LAROMER PE 55 w	parts 0.95
Product of example 1	parts 0.045

TH the finished are applied on an asbestos cement panel to a thickness of 250 micrometers (wet).

Tryed in darkness and then exposed to the sun light for 3 days in order that the absorbed energn[2] at 340 nm.

Tls are reported in Table 5

TABLE 5

acteristic	Base	Finished
appearance	polished compact	polished compact
:r repellency (Spray test)	totally wettable	impermeable
:r resistance (100 double rubs)	matted	unchanged
resistance (100 double rubs)	matted	unchanged
resistance (suspension Fe_2O_3)	brown	colourless
stance to 2 double bending	unchanged	unchanged

the re that the photoinitiators in aqueous disperse systems of the present invention can be advansed in the resin dispersions (water-paint) for the building industry (or similar) to impart betterto the coatings.

Itoticed that films containing the photopolymerisable resin and the photoinitiator show better supernce thanks to the spread crosslinking without losing in flexibility.

EXAN

To a wood-lacquer, consisting of 36.5 parts of acrylated polyester and 6.5 parts of rutile titanium bioxide dispersed in 57 parts of water, are added 4.3 parts of a dispersion of photoinitiator (I) according to Example 1 (PID A) but containing also 4.3 parts of 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide for 100 parts of PID A (PID A + APO). After agitation for 5 minutes and degasing for 4 hours the lacquer is applied to a thickness of 200 micrometers (wet), the water is evaporated for 20 minutes at 65° C and the resulting film is irradiated with a 80 W IST lamp (distance from the lamp 29 cm) at 3 m/min by three passages. After 4 hours the properties reported in Table 6 are measured and compared with the properties of films obtained by introducing the photoinitiators (II):

TABLE 6

Phot.	Parts % on system	Parts % phot. resin	Hard. Koenig (sec)	Mek (doub. rubs)	Appea.	Resist. nail-scratch
(I)PID A+APO	4.3	-	-	-	-	-
KIP	-	4	45	>300	White polis.	Total
APO	-	0.5	-	-	-	-
(II) KIP	2	4	-	-	-	-
APO	0.18	0.5	22	180	White	Scratch rough surface grains

The example shows that it is possible to obtain a total crosslinking also in the depth of strongly pigmented films prepared from aqueous disperse systems using dispersed photoinitiators, while using commercially available products the properties obtained are not useful for practical use.

EXAMPLE 10

In this example are compared the properties of films obtained from two photocrosslinkable compositions containing the same photoinitiator (ESACURE KIP) and the same oligomer (ROSKYDAL 850 w -acrylated autoemulsifying polyester - Bayer) but differing in so far as the diluent is concerned.

In one case the diluent is water (emulsified composition) in the other case is hexadiolacrylate (reactive diluent monomer, HDDA). The liquid mixtures are applied to glass in order to obtain crosslinked films to a thickness of 100 micrometers, after evaporation of water in oven at 100° C for 10 minutes and crosslinking through irradiation with a 80 W Hanovia 6512-A-431 lamp (distance from the lamp 10 cm) (2 passages).

On the crosslinked film are evaluated: hardness (Koenig's pendulum DIN 53157), residual smell, weight lost and the extract in diethyl ether, as reported in Table 7.

The example shows that an emulsified system permits to obtain characteristics similar to those of photocrosslinkable systems diluted in a reactive solvent but permits also to avoid the presence of smell and residual monomer in the crosslinked films.

TABLE 7

Components (mixed according to the given order)	A	B
1. ROSKYDAL 850 w	100	60
2. HDDA	-	40
3. ESACURE KIP	-	2
4. Water	60	-
5. Product of example 1	4.4	-
Applied thickness wet (nanometer)	160	100
Hardness (Koenig) (sec)	60	65
Smell (1)	absent	strong
Weight loss at 120 °C	0.05%	2.5%
Extract in diethyl ether	absent	2.7% (2)

(1) The residual smell is totally independent from the photoinitiator which, being oligomer, gives no photolytical fragments volatile or smelling.
(2) The infrared spectroscopy analysis shows that the extracted is prevalently HDDA.

Claims

1. Aqueous disperse systems of photoinitiators comprising at least a photoinitiator and at least a surface active agent, wherein the photoinitiator represents from 20% to 80% by weight and the surface active agent from 0.1% to 10% by weight of the disperse system.

2. Aqueous disperse systems of photoinitiators according to claim 1, wherein that the photoinitiator represents from 30% to 60% by weight of the disperse system and the surface active agent from 0.5% to 2% by weight.

3. Aqueous disperse systems according to claim 1, wherein the photoinitiator is a compound chosen in the group of benzoine ethers, benzyl-dimethyl-ketal, 2,2-di-alkoxy-acetophenones, alpha-hydroxy-alkyl-aryl ketones, arylglyoxylic acids esters, mono- and di-acyl-phosphine oxides, or their mixture; or aromatic ketones, tioxanthones, antraquinones or their mixture; or hexa-aryl-bis-imidazoles.

4. Aqueous disperse systems of photoinitiators according to claim 1, wherein the photoinitiator is coupled with an hydrogen donor (coinitiator), the weight ratio between the photoinitiator and the hydrogen donor (coinitiator) is comprised between 1:1 and 1:2.5.

5. Aqueous disperse systems of photoinitiators according to claim 3 wherein the photoinitiator is benzophenone or its alkyl derivatives.

6. Aqueous disperse systems of photoinitiators according to claim 4, wherein the hydrogen donor (coinitiator) is a compound containing a tertiary amino group with at least an hydrogen atom on the carbon atom linked to the nitrogen of the amino group.

7. Aqueous disperse systems of photoinitiators according to claim 6, wherein the hydrogen donor (coinitiator) is a compound chosen in the group consisting of N-methyl-N,N-diethanolamine (MDEA), triethanolamine, p-dimethylamino-benzoic acid esters.

8. Aqueous disperse systems of photoinitiators according to claim 1, wherein the surface active agent is chosen in the group consisting of : organic sulphonic acids and their salts, mono-alkyl sulphates, quaternary ammonium salts, higher aliphatic alcohols or alkyl-phenols condensed with ethylene oxide and/or propylene, partial esters of phosphoric acid with aliphatic alcohols and their salts.

9. Aqueous systems of photopolymerisable oligomers and/or polymers mixed with an aqueous disperse systems of photoinitiators as described in the above claims in such a quantity that the ratio of the dry part in the dispersion and in the system is comprised between 0.5 and 100% by weight of system.

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(71) Applicant: **FRATELLI LAMBERTI S.p.A.**
Via Piave 18
I-21041 Albizzate (Varese)(IT)

(72) Inventor: **Li Bassi, Giuseppe**
Via Stretti, 4
I-21026 Gavirate (Varese)(IT)
Inventor: **Nicora, Carlo**
Via Filzi, 2
I-21100 Varese(IT)

(74) Representative: **Gervasi, Gemma et al**
NOTARBARTOLO & GERVASI Srl Viale Bianca Maria 33
I-20122 Milan(IT)

(54) **Aqueous disperse systems of photoinitiators and their use.**

(57) The invention relates to aqueous disperse systems of photoinitiators which are particularly useful in the photopolymerisation of aqueous disperse systems and emulsions of oligomers or polymers carrying photopolymerisable functionalities which are widely used in the field of dyes and packaging.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 341 534 (MERCK PATENT GmbH) * Claims 1-4,8; page 2, line 43; page 3, lines 7-24 *	1-9	C 08 F 2/50 G 03 F 7/031
D,X	EP-A-0 085 305 (MERCK PATENT GmbH) * Claims 1,2; page 2, lines 1-16; page 10, lines 21-31; page 14, lines 12-15 *	1-3,9	
D,X	WO-A-8 605 778 (MERCK PATENT GmbH) * Claims; page 15, lines 23-32; page 16, lines 14-33 *	1-9	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 08 F
G 03 F

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	03 June 91	METTLER R.M.

CATEGORY OF CITED DOCUMENTS

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